Potato Starch Factory Waste Effluents

II. Development of a Process for Recovery of Amino Acids, Protein and Potassium[a]

E. G. Heisler, J. Siciliano and S. Krulick

Eastern Regional Research Laboratory, Eastern Marketing and Nutrition Research Division, ARS, U.S. Department of Agriculture, Philadelphia, Pennsylvania 19118

Problems associated with the secondary waste effluents from potato starch factories and the basic studies leading to a proposed ion-exchange process for the treatment of such wastes to decrease the biochemical oxygen demand (b.o.d.) by removal of protein and amino acids are discussed. The variables studied and the data needed for design of a process are reported.

Five products are obtained: (i) a basic amino-acid mixture containing approximately 30% arginine, 8% lysine and 6% histidine; (ii) an acidic and neutral amino compound mixture containing approximately 30% asparagine; (iii) potato protein; (iv) a fertiliser product having an n.p.k. of 12-0-22; and (v) a liquid fertiliser containing 8% ammonium sulphate.

By the removal of these constituents the b.o.d. is decreased approximately 60%.

1. Introduction

The problem of stream and ground water pollution by waste effluents from food processing plants has become one of major importance in the United States. The starch production segment of the potato processing industry contributes considerably to this problem because everything except starch is considered as waste and must be handled in some way to prevent pollution.

The secondary (soluble) wastes from these starch factories consist of relatively low concentrations of organic and inorganic materials in large volumes of water. Their composition, on a dry weight basis, is roughly as follows: 15% protein; 30% amino compounds; 30% organic acids; 15% reducing sugars and 10% potassium. The biochemical oxygen demand (b.o.d.) of this mixture is extremely high and, therefore, requires an efficient type of sewage or other waste treatment. The potato starch industry is, in itself, a disposal operation since it uses as raw materials only those tubers which cannot be utilised in a more profitable way. As a result of competition from other domestic and imported starches, the industry operates on a narrow profit margin and, therefore, cannot absorb added waste treatment costs.

We have developed in the laboratory a system for recovering materials from such waste, thereby reducing the effluent b.o.d. and, by their sale, providing a means of recovering some of the cost of treatment. The proposed system would consist of five

[a] Part I in this series is: *Am. Potato J.* 1970, **47**, 326.

steps: (i) concentration of dilute waste to at least 2.5% total dissolved solids (t.d.s.) or institution of changes in in-plant use of water to produce a more concentrated effluent; (ii) an initial ion-exchange treatment that accomplishes three things: precipitates protein, recovers a fertiliser mixture consisting of potassium and other minor inorganic cations and recovers a basic amino-acid mixture containing approximately 30% arginine; (iii) recovery of precipitated protein from effluent of step (ii); (iv) a second ion-exchange treatment to remove the bulk of the free amino acids. This step yields a mixture containing mainly the acidic and neutral amino compounds, asparagine being the main one; (v) a third ion-exchange treatment to remove the organic acids, which will be described in another paper.

Previous publications from this Division have discussed the reverse osmosis concentration of the effluent,[1] heat coagulation and recovery of protein,[2] the recovery of potassium and other cations[3] and the laboratory scale removal of amino compounds by ion-exchange,[4,5] as well as an economic study of five alternative processes of starch plant waste treatment.[6] This publication will deal with steps (ii), (iii) and (iv) of the above process. First, it presents a modification of the previously described potassium recovery step,[3] to include the recovery of two additional products, protein and a basic amino-acid mixture containing approximately 30% arginine. Second, it describes the recovery of the bulk of the free amino acids by a second ion-exchange treatment. Basic and practical data required for evaluating the commercial possibility of the laboratory process are presented. These data include a comparison of the effectiveness of two types of strong acid type cation exchange resins, a more elaborate study of the effect of solids concentration in the waste and a study of operation variables such as temperature, rate of flow and direction of flow. A continuous procedure using a three-column system is also described.

2. Experimental

All ion-exchange studies were performed using 1 in (25.4 mm) diameter, 36 in (0.3048 m) long, water-jacketed, glass columns containing 300 ml of wet cation exchange resin with a void volume of 150 ml. The 1 in. (25.4 mm) columns were used on the advice of a manufacturer of ion exchange resins that they would supply all the information required for enlarging to commercial scale. Two types of strong acid cation exchange resins were studied.[a] One, IR 120,[b] is an example of the standard, commercially available resin. The other, XE 252, is an example of the newer macroreticular resin now commercially available. Exhaustion and elution were monitored by conductance recording of the flowing streams. Constant-flow pumps were employed for all streams; waste input, wash water and eluting agents. Total content of amino compounds was determined by use of the Stein–Moore reagent[7] with asparagine as the standard. Individual amino compounds were determined by an automatic amino-acid Analyzer.[8] The dichromate reflux method[9] was employed for estimating the chemical oxygen demand (c.o.d.) of the treated and untreated waste water. Total dissolved solids content (t.d.s.) was ascertained by drying in a forced draft oven at 90 °C to constant weight.

[a] Kindly furnished by the Rohm and Haas Company, Philadelphia, Pa.
[b] Mention of company or trade names does not imply endorsement by the Department over others not named.

3. Results and discussion

3.1. Modification of the initial ion-exchange treatment step

A previous publication from this laboratory[3] proposed a process for recovering inorganic cations (mainly potassium) from the potato starch factory waste effluents as a prelude to recovery of the amino acids. Removal of the inorganic cations (mainly potassium) from the waste water prior to amino-acid removal increases the capacity of the column for amino compounds and also results in a more favourable exchange rate. Data in previous publications[4,5] indicated the capacity of a 300-ml column to be 20 to 25 g of amino compounds with waste containing the inorganic cations. Data from this work indicate the capacity to be 40 to 60 g when the inorganic ions are previously removed. Further experimentation has established the desirability of modifying the procedure. First, it has been found to be feasible to precipitate the protein as part of the ion-exchange process, thus eliminating a preliminary protein removal step. When potato starch plant waste water that contains the soluble protein is passed through the cation exchange column (H^+ form) the protein is precipitated, due to a lowering of the pH of the effluent to approximately 2.0. The requirement noted earlier for an essentially protein-free input to the column was based on conventional downflow technique. If an upflow technique with a fast flow rate of 30 bed vol./h (b.v./h) was employed clogging of the column did not occur when the protein was not previously removed. These are the conditions used in the potassium removal step. This fast flow rate expanded the bed volume 1.5 times and thus kept the resin in good motion. The protein precipitated in the column as a fine suspension and was flushed out continuously without any difficulty. This precipitation technique removes about 80% of the original soluble protein. The remaining 20% is soluble in an acid medium. Most of it is adsorbed on the column and eluted with the basic amino acids. The rest is adsorbed during the next step and is found in the acidic and neutral amino-acid mixture.

The effluent from the column containing the acidic and neutral amino acids, the organic acids, the sugars and the precipitated protein is fed into settling tanks where the precipitated protein settles to the bottom and is drawn off as a relatively concentrated slurry containing approximately 6% protein. This slurry is further dewatered

TABLE 1. Amino-acid content of potato protein

Amino acid	m.f.b. %	Amino acid	m.f.b. %
Aspartic acid	10.3	Glycine	3.9
Glutamic acid	8.3	Alanine	3.8
Leucine	7.9	Arginine	3.6
Lysine	5.4	Proline	3.0
Phenylalanine	5.0	Histidine	1.9
Threonine	4.9	Methionine	1.8
Valine	4.7	Ammonia	1.3
Isoleucine	4.6		
Tyrosine	4.4		
Serine	3.9	Total	78.7

by centrifugation to a moist protein cake containing approximately 66 % moisture. The protein cake can be dried by any conventional technique. The protein obtained by the above procedure is not pure. It contains small amounts of free amino acids, organic acids and sugars. Using the three column process proposed in a previous publication[3]

TABLE 2. Outline of process for recovering protein, fertiliser and basic amino acids

Exhaustion or loading step

Fraction being collected off scav. col.	Liquid being pumped 2.6 % t.d.s. 30 b.v./h (52 min) volume, b.v.	Composition	Disposition
Void	1.0		To waste
Eff.	25.0	2.2 % t.d.s. (before protein removal)	To protein removal unit
		1.4 % t.d.s. (after protein removal)	Supernatant and centrifugate to step (iv) input

Basic elution step

Fraction being collected off main column	Liquid being pumped 25 b.v./h (13 min) volume, b.v.			Composition	Disposition
		$BE_1{}^a$	$BE_0{}^b$	H_2O		
Lowering of head	0				(2.6 %) t.d.s.	Recycle to feed
	1					
Eff. wash				0.50	(<2.6 %) t.d.s.	Recycle to feed
Void		0.75			(<2.6 %) t.d.s.	Recycle to feed
Middle		1.25			2.5 % basic amino acids	To dryer (product)
Tailing			1.0	1.0	(<0.77 %) basic amino acids	Becomes BE_1

Acid elution step (regeneration)

Fraction being collected off main column	Liquid being pumped 10 b.v./h (33 min) volume, b.v.			Composition	Disposition
		$AE_1{}^c$	$AE_0{}^d$	H_2O		
Void		0.75			5.8 % K_2SO_4 $\xrightarrow{NH_3}$	Fertiliser product
Middle		1.25	0.25		6.3 % $(NH_4)_2SO_4$	NPK of
					1.5 % H_2SO_4 (Neut)	12-0-22
Tailing			0.75	1.25	(10 %) H_2SO_4	Becomes AE_1

^{a} BE_1, is once recycled NH_4OH, 2 N.
^{b} BE_0, is fresh NH_4OH, 3 N.
^{c} AE_1, is once recycled H_2SO_4, 2 N.
^{d} AE_0, is fresh H_2SO_4, 3 N.

and modified in this publication (see Table 2), a potato starch plant producing 30 tons[a] of starch/16 h day and having an effluent of 6,750 gal[a]/h (30,712 l/h) containing 2.6% t.d.s. would yield approximately 1.5 tons dry protein/16 h day. This is based on a protein content of 17% of the t.d.s. and a yield of 80%. The protein was hydrolysed and analysed for individual amino-acid content using the automatic amino-acid Analyser.[8] Table 1 gives the results obtained.

A second modification of the previously described process involves the recovery of a basic amino-acid mixture, mainly arginine, histidine and lysine. Experimentation has shown that when using resin XE 252 (a strong acid cation resin of the macroreticular type) all the amino acids are not displaced by the potassium. Even when a very large excess of waste is put through, containing more than enough potassium to load the column, about one-third of the capacity of the column is occupied by basic amino acids. Surprisingly, it was found that the basic amino acids are not eluted with sulphuric acid; however, they are eluted with 2 N-NH_4OH. On the other hand, the potassium is eluted with 2 N-H_2SO_4 but not NH_4OH. It is therefore recommended that the process proposed in the previous publication[3] be modified to include an NH_4OH elution step prior to the elution of the potassium with H_2SO_4. This necessitates a change in the elution schedule. The proposed schedule is shown in Table 2. Based on the 30 ton/day potato starch plant, this process would yield about 0.6 ton of the crude basic mixture (see Table 3) and 1.0 ton of potassium/day. Translating the potassium yield to the fertiliser product (ammonia neutralisation) yields a weight of 5.0 ton of fertiliser/day. The makeup of the basic amino-acids mixture is given in Table 3.

TABLE 3. Analysis of basic mixture

	m.f.b. %		m.f.b. %
Arginine	30.62	Tyrosine	1.85
Lysine	8.32	Phenylalanine	1.55
Histidine	6.08	Tryptophan	0.63
Asparagine	3.18	11 other amino acids	2.4
γ-NH_2-n-Butyric	2.04	Ash	2.13

3.2. Separation and recovery of remaining amino compounds

3.2.1. Exhaustion or loading step

A comparison of the performance of the two resins was made under varying conditions of temperature and flow rate. Concentration history curves[10] were obtained under the conditions studied. These curves are a plot of the ratio of concentration of the effluent to concentration of the influent (C/C_0), both with respect to amino compounds, against put-through volume of waste effluent or weight of constituent (grams treated). This curve shows the fraction of a constituent being exchanged by the resin at any stage during the exhaustion step. The C/C_0 value, when multiplied by 100, is equal to the

[a] Throughout this paper 1 ton ≈ 1020 kg, 1 gal ≈ 4.55 l.

percent leakage. In the beginning, when practically all of the amino compounds are being adsorbed, the C/C_0 value is near zero, the leakage is near zero, making the column effluent essentially free of amino compounds. At the end of the exhaustion cycle, as the C/C_0 value approaches 1, the column is saturated, the leakage is approaching 100% and the column effluent is almost identical with the influent. The data for the curves in Figure 1 were obtained at room temperature with waste water containing 2.3% t.d.s. and 0.52% amino compounds. Figure 1 compares the two resins at a flow rate of 10
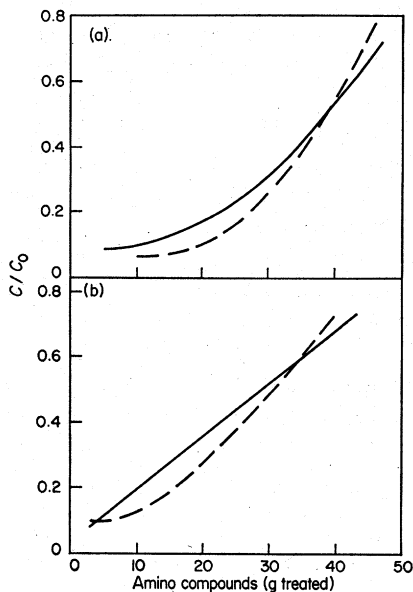
Figure 1. Comparison of resins at room temperature. Waste of 2.3% t.d.s., 0.52% amino compounds. (a) Rate 10 b.v./h; (b) rate 20 b.v./h. ——, IR 120; – – –, XE 252.

b.v./h and 20 b.v./h. It is readily apparent that, for both flow rates at room temperature, XE 252 is superior to IR 120. For example, if a leakage level of 20% is arbitrarily selected as a reference point, the capacity (grams treated) at 10 b.v./h is 22.5 and 27.5 g of amino compound for the IR 120 and XE 252 resins, respectively. At 20 b.v./h it is 10.5 and 15.8 g. The effect of elevated temperature on the exchange is shown for both resins in Figure 2, using flow rates of 10 b.v./h and a feed containing 2.1% t.d.s. and 0.6% amino compounds at 45 and 65 °C. The data show that, compared with room temperature, there is an increase in efficiency of both resins at 45 °C since the capacity (grams treated) at 20% leakage is 35 g of amino compounds for both resins. The efficiency at 65 °C is not significantly better than at 45 °C. At elevated temperatures, therefore, the two resins are about equal in their ability to exchange amino compounds. From this comparison study it can be stated that, if the recovery is carried out at room temperature the XE 252 resin would be preferable from the efficiency viewpoint; if elevated temperatures are employed either resin would be acceptable.

The effect of t.d.s. content of the feed on the exchange rate and the efficiency of the operation was determined using XE 252 and room temperature feed. In this study the t.d.s. content was used rather than total amino compound content because it is the value that would be most readily available at the plant. The t.d.s. content of the waste water is the primary value by which the waste water is evaluated and it can be readily related to the c.o.d. (b.o.d.) of the waste water. For example, 1% t.d.s. is equivalent to a c.o.d. value of about 10 000 parts/million. For these reasons it was
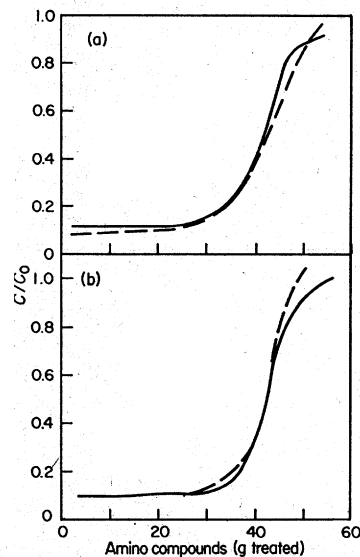
Figure 2. Comparison of resins at elevated temperatures. Flow rate 10 b.v./h, 2.1% t.d.s., 0.6% amino compounds. (a) 45 °C; (b) 65 °C. ——, IR 120; – – –, XE 252.

thought advisable to express the capacity of the column in terms of g of t.d.s. treated and the "treatment rate" as g of t.d.s. treated/h. The analysis of many samples of potato waste water from many varieties and locations show that in 90% of the samples the total amino compound content was in the range 23% to 35% of the t.d.s. The amino compound content of the waste water used in the following study was 30.5% of the t.d.s.

To make this study, four series of experiments (three experiments/series) were run. Each series was conducted under constant "treatment rate" conditions (g of t.d.s. treated/ h), as the t.d.s. content was reduced the flow rate was increased as indicated in Table 4. Concentration history curves were constructed. The curves obtained for one of the series are shown in Figure 3 (others not shown). From the concentration history curves, the capacity in g of t.d.s. treated (to 20% leakage) was obtained. These values are listed in Table 4. From the data in this table a graph was constructed (Figure 4) which shows the relationship of flow rate to capacity in g of t.d.s. treated (to 20% leakage). This plot shows that if only flow rate is considered ("treatment rate" allowed to decrease at lower % feed is employed) the % t.d.s. has little effect on the capacity. For example, at 10 b.v./h the t.d.s. content of the feed can be lowered from 2.14 to 0.93% without

TABLE 4. Effect of t.d.s. content of feed on capacity and efficiency of operation

| Flow rate | | t.d.s. of waste | Treatment rate | Capacity (to 20% leakage) | Min. waste water that can be treated |
b.v./h	ml/min	%	g of t.d.s./h	g of t.d.s. treated	% t.d.s.
10	50	0.93		104	
15	75	0.62	27.9	81	0.86
30	150	0.31		43	
10	50	1.10		107	
15	75	0.73	33.0	90	0.97
30	150	0.37		50	
10	50	1.84		104	
20	100	0.94	55.2	72	1.62
40	200	0.47		31	
10	50	2.14		102	
20	100	1.07	64.2	63	1.98
40	200	0.53		28	

Figure 3. Concentration history curves obtained under conditions of constant treatment rate and varying % t.d.s. Resin XE 252, treatment rate 55.2 g of t.d.s./h, feed at room temperature.

any appreciable decrease in capacity. Thus low % t.d.s. waste water can be treated but at the expense of "treatment rate" or efficiency. To obtain a quantitative measure of this loss of efficiency with decreasing t.d.s. content of waste water the following treatment of the data was undertaken. In Figure 5 the capacity values (g of t.d.s. treated to 20% leakage) are plotted against % t.d.s. of feed under conditions of constant "treatment rate". Four curves are shown, one for each of the four treatment rates. This demonstrates graphically that under conditions of constant treatment rate the lower the % t.d.s. of feed the lower the capacity of the column. From the curves shown the minimum concentration of feed that can be treated at a given treatment rate at an assigned acceptable level of capacity (to 20% leakage) can be determined. For example, with 100 g

of t.d.s. chosen as an acceptable capacity at a treatment rate of 64.2 g of t.d.s./h, the minimum % t.d.s. feed that can be treated is 1.98%, that is, waste water containing 1.98% t.d.s. and above can be treated. At a lower treatment rate of 55.2 g of t.d.s./h waste water containing as little as 1.62% t.d.s. can be treated. The minimum t.d.s. values
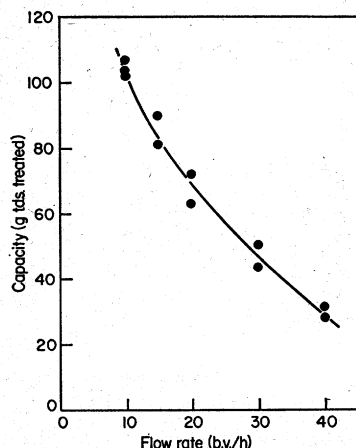

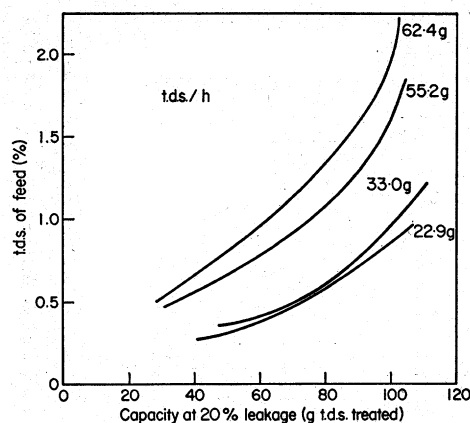Figure 4. Capacity as related to flow rate. T.d.s. content varied from 2.14% to 0.31%. Resin XE 252, feed at room temperature.

Figure 5. Capacity as related to % t.d.s. of feed under conditions of constant treatment rate. Resin XE 252, feed at room temperature.

obtained are listed for the convenience of the reader in Table 4. To obtain a continuous relationship between treatment rate and minimum % t.d.s. feed that can be treated the graph shown in Figure 6 was plotted. From this plot the proper treatment rate can be obtained for a given % t.d.s. content of waste water and from the treatment rate the flow rate can be determined using the following formula; b.v./h = treatment rate/ 3X (% t.d.s.). This curve thus can be used to determine the column size that would be required to treat the effluent from a potato starch plant.

If the recovery process is carried out using an upflow technique for the exhaustion (or loading) step the need for backwashing would be eliminated and clogging of the column would be prevented. For this reason, experiments were carried out to determine if direction of flow affected the exchange rate. The two techniques were compared
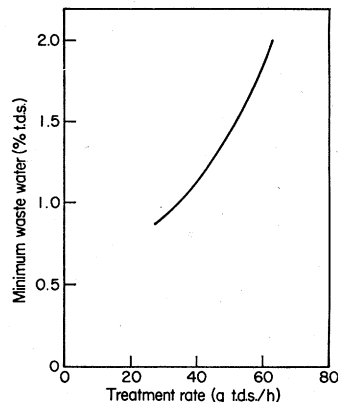

Figure 6. Relationship of treatment rate to minimum % t.d.s. that can be treated under conditions of acceptable capacity level. Resin XE 252, feed at room temperature.

directly using the same feed under exactly equal conditions of temperature and flow rate. The XE 252 resin was used. The data presented in Figure 7 indicate that an upflow technique could be used without appreciable sacrifice of efficiency; in fact, an upflow technique results in less initial leakage since regeneration is by downflow.
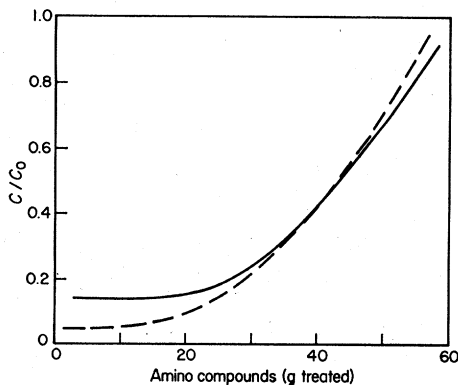

Figure 7. Comparison of effect of direction of flow on exchange rate. Resin XE 252, 2.0% t.d.s., feed at room temperature. ——, Down flow; – – –, up flow.

3.2.2. Elution step

Ammonium hydroxide is used for the elution of the amino compounds from the loaded exchange columns. The effects of NH_4OH concentration and flow rate on the elution were presented in a previous publication[4] and 2 N-NH_4OH was tentatively established

as the optimum concentration. To obtain further data on the effect of these two variables a series of experiments was conducted, using 2 N-NH₄OH, in which the flow rate was varied from 2 to 10 b.v./h. All other variables related to the loading and elution of the column were kept constant. The XE 252 column was loaded to saturation using upflow with waste of 1.4% t.d.s. Periodically during the downflow elution, 5-ml samples of the eluate were taken and amino compound content determined. The elution curves
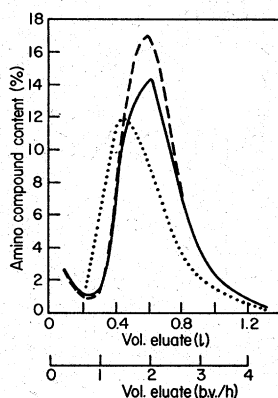

Figure 8. Effect of eluent flow rate on concentration of amino compounds. Resin XE 252, room temperature, eluent 2 N-NH₄OH. ——, 5 b.v./h; – – –, 2 b.v./h; ·····, 10 b.v./h.

are presented in Figure 8 where amino compound content is plotted against eluate volume. The data show that the height of the peak increases with decreased flow rate. In Table 5 are listed some points to consider, such as (i) the maximum concentration of amino compound attained, (ii) the volume of eluate that contained at least 3%

TABLE 5. Effect of flow rate and NH₄OH concentration on elution

Flow rate, b.v./h NH₄OH Concentration	10 2 N	5 2 N	4 N	2 2 N
Max. amino content attained (%)	11.8	14.2	22.6	16.9
Vol. eluate containing at least 3% amino compounds (ml)	580	600	410	600
Total weight amino compounds eluted in above volume (g)	44.3	52.6	52.6	61.2
Amino compound content of above volume (%)	7.6	8.8	12.8	10.2
Weight NH₃ required to elute the amino compounds to 3% level (g)	—	31.9	48.2	—

amino compounds, (iii) the total weight of amino compounds eluted in this volume and (iv) the content of amino compound in this volume. The total weight eluted and the amino compound content were obtained by determination of the area under the curve.

The volume of eluate remains fairly constant; however, the total weight eluted increases with decreased flow rate indicating that the faster flow rates give incomplete elution. In Figure 9, the peak value and the amino compound content of the eluate is plotted against flow rate. The curves show an increase in amino compound content with a
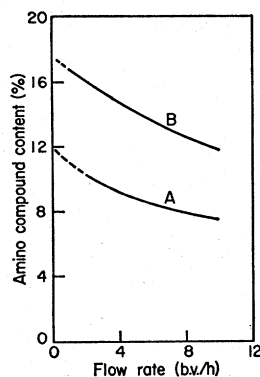

Figure 9. Effect of flow rate on amino compound content of eluate. A, amino compound content; B, maximum amino compound content.

decrease in flow rate. Use of as low a flow rate as economically possible would, therefore, be advantageous. However, in a continuous process the elution flow rate would be somewhat governed by the running time of the loading step.
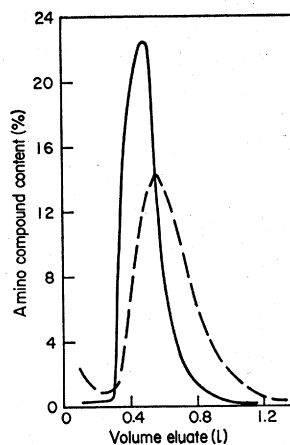

Figure 10. Effect of concentration of NH_4OH on elution curves obtained at 5 b.v./h. Resin XE 252, 1.4% t.d.s. feed at room temperature. ——, 4 N-NH_4OH; – – –, 2 N-NH_4OH.

Using a flow rate of 5 b.v./h and the above loading and sample conditions, 2 N and 4 N-NH_4OH were compared as eluting agents. Figure 10 presents the elution curves obtained and the variables considered are listed in Table 5. The higher concentration elutes the same weight of amino compounds in a smaller volume; thus the maximum

and the amino compound content is higher. However, from an efficiency standpoint it is seen that more NH_3 on a weight basis is required to reach the same degree of elution when 4 N is used. For example, to reach the level of elution where the amino compound content of the eluate has dropped to 3% required 31.9 g of NH_3 with 2 N (940 ml) and 48.3 g with 4 N (710 ml).

3.2.3. Regeneration step

After elution of the amino compounds with NH_4OH the column is, of course, in the $[NH_4]^+$ form and must be converted to the $[H]^+$ form by use of 2 N-H_2SO_4 before it can be re-used in the next amino compound loading cycle. Concentration history curves with C/C_0 values, in terms of mequiv. H_2SO_4, are presented in Figure 11 for
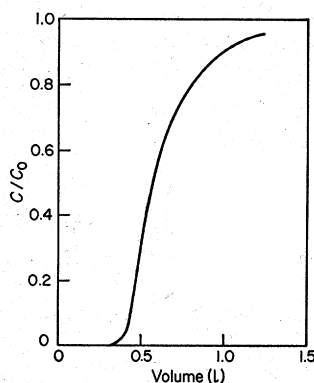

Figure 11. Regeneration of column with 2 N-H_2SO_4, effect of flow rate. Resin XE 252, 1.4% t.d.s. feed at room temperature.

flow rates of 2, 5, and 15 b.v./h. Since the curves coincide it is obvious that flow rate is not critical in this step, an advantage when scheduling operations. The time available for elution and regeneration will equal the time required to load the column. Thus, regeneration at a fast flow rate will allow more time for elution.

4. Proposed process

Based on the experimental work reported above a three-column continuous process is proposed. The details are outlined in Table 6. The elution and regeneration schedule shown is one that involves the use of recycled and fresh NH_4OH and H_2SO_4. Recycling eliminates the loss of partially spent eluent or regenerant and employs the least amount of fresh reagent. For the basic elution and the acid regeneration, a total of 2910 mequiv. of base and acid is used/cycle. This is approximately 6.5 times the column capacity but it should be emphasised that only 900 mequiv. of this is fresh input into the system/ cycle. Three columns are used to make the process continuous. In any one cycle, one column is being loaded, the next is acting as a scavenger to trap amino compounds leaking from the loading column and the third is being eluted. For example, if the three columns are labelled A, B and C and in cycle X column A is the main column, column

TABLE 6. Outline of process for recovering amino compounds

Exhaustion or loading step

Fraction being collected off scav. col.	Liquid being pumped (waste water cont. 1.4% t.d.s., 0.4% amino compds.) 10 b.v./h Volume (b.v.)	t.d.s.	Composition (%) Amino compds.	$(NH_4)_2SO_4$	H_2SO_4	Disposition
Void	1.0	0.9	—	0.4	0.5	To waste
Eff. (amino compd-free)	40.0	1.0	0.07	—	—	To organic acid recovery unit

Basic elution step

Fraction being collected off main column	$BE_2{}^a$	$BE_1{}^b$	$BE_0{}^c$	H_2O	Total	t.d.s.	Amino compds.	NH_3	Disposition
Eff. wash				0.50	0.50	1.2	0.42		Rtn. to waste input
Void	1.00	0.33			1.33	0.7	0.28	0.3	Rtn. to waste input
Middle		1.00			1.00	13.5^g	(14.9)		To dryer
Tailing, 1		1.00			1.00	2.0^g	2.0	3.1	Becomes BE_2
Tailing, 2			1.00	1.33	2.33	0.2^g	0.2	3.6	Becomes BE_1
Total	1.00	2.33	1.00	1.83	6.16				

(Liquid being pumped (2 b.v./h), Volume (b.v.); Composition (%))

Acid regeneration step

Fraction being collected off main column	$AR_2{}^d$	$AR_1{}^e$	$AR_0{}^f$	H_2O	Total	t.d.s.	$(NH_4)_2SO_4$	H_2SO_4	Disposition
Void	1.00	0.33			1.33	8.1^h	8.1^h	2.0	Secondary product, $(NH_4)_2SO_4$ soln— liquid fertiliser
Middle		1.00			1.00				
Tailing, 1		1.00			1.00	11.2	1.9	9.3	Becomes AR_2
Tailing, 2			1.00	1.33	2.33	11.2	0.9	10.3	Becomes AR_1
Total	1.00	2.33	1.00	1.33	5.66				

(Liquid being pumped (7 b.v./h), Volume (b.v.); Composition (%))

[a] BE_2 is twice recycled NH_4OH, 3.1% NH_3 (1.8 N).
[b] BE_1 is once recycled NH_4OH, 3.6% NH_3 (2.1 N).
[c] BE_0 is fresh NH_4OH, 5.1% NH_3 (3.0 N).
[d] AR_2 is twice recycled H_2SO_4, 9.3% H_2SO_4 (1.9 N).
[e] AR_1 is once recycled H_2SO_4, 10.3% H_2SO_4 (2.1 N).
[f] AR_0 is fresh H_2SO_4, 14.7% H_2SO_4 (3.0 N).
[g] t.d.s. after free NH_3 has been evaporated.
[h] % after neutralisation.

B the scavenger and column C is being eluted and regenerated, then in cycle Y, column B becomes the main column and C the scavenger and column A is eluted and regenerated. In cycle Z, C is the main column, A is the scavenger and B is eluted and regenerated. Use of a scavenger permits the column to be loaded almost to saturation. The main column is operated upflow and the scavenger is operated downflow. Scavenger is

run downflow for convenience and economy of operation. Air (or gas) would be a problem if effluent from main column entered through the bottom of the scavenger column. Downflow operation of the scavenger thus eliminates the need to install bubble traps between the columns.

The amino-acid removal process was carried out continuously using the three-column procedure. By the third cycle, conditions had stabilised and the data in Table 6 can be considered typical of that which would be obtained in a commercial process.
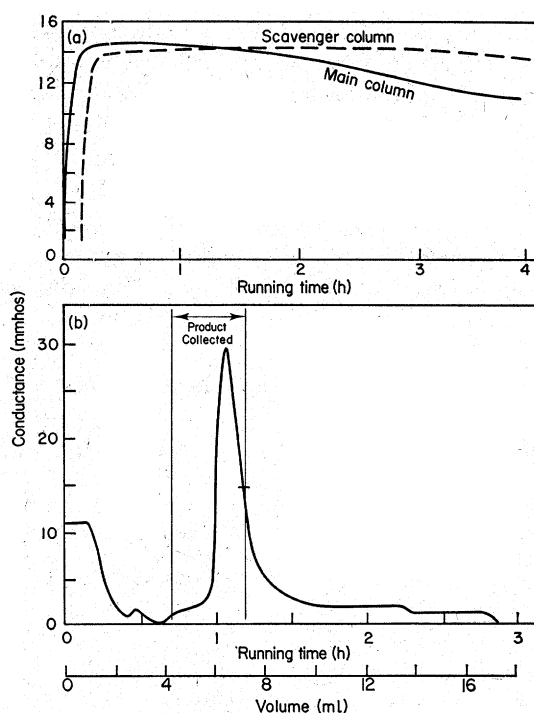

Figure 12. Conductance curves. (a), Loading curves, flow rate 10 b.v./h; (b), Basic elution curve, flow rate 2 b.v./h.

Both column loading and elution were monitored continuously by conductance measurements on the flowing liquid. Figure 12 presents the conductance curves obtained for the two steps. The main column loading conductance curve shows a gradual decrease in conductance with a gradual levelling off of the rate of decrease as the column becomes saturated. The scavenger curve shows a constant conductance as long as only minimal leakage occurs. When this curve begins to decrease noticeably, indicating an increased leakage rate, the loading of the main column is terminated. The basic elution curve is also presented in Figure 12. The part of the curve where the product is collected is indicated. The acid regeneration step was not monitored.

The waste water used originally contained 2.59% t.d.s. After removal of protein, inorganic ions and basic amino acids by the first ion-exchange treatment, the t.d.s. decreased to 1.38% and the waste water contained 0.40% amino compounds on a wet

basis or approximately 30% on a moisture free basis. As shown in Table 6, it required 40 b.v. (12 l) of this waste water to saturate the column using a flow rate of 10 b.v./h. The loading step thus required 4 h. The data show some leakage even when a scavenger is used. The "amino compound-free waste water" contains a small amount (0.07% wet basis) of amino compounds which are mainly aspartic and glutamic acids.

On elution with NH_4OH at 2 b.v./h, one b.v. of a concentrated amino-acid mixture (13.5%) was obtained/cycle. The cut-off is made at 1 b.v. even though at this point the amino compound content is still approximately 9% (but dropping rapidly—see elution conductance curve on Figure 12). This is done to attain the high 13.5% amino compound content of the product and also to keep the input of fresh 3 N-NH_4OH at the low level of 1 b.v. In a continuous operation the "take out" from the system must equal the "input" into the system. There is no loss of amino compounds since the eluate beyond the cut-off point is recycled. The analysis of the 1 b.v. of product for individual amino acids is given in Table 7. Regeneration of the column with H_2SO_4 at 7 b.v./h produced 2.33 b.v. of eluate containing 5.4% $(NH_4)_2SO_4$ and 2.0% H_2SO_4. On neutralisation with NH_3 an 8.1% solution of $(NH_4)_2SO_4$ is obtained. Running time for the combined elution and regeneration step averaged 3 h 50 min. This schedule would allow for continuous loading.

TABLE 7. Analysis of amino compound mixture

Amino acid	m.f.b. %	Amino acid	m.f.b. %
Asparagine plus glutamine	30.6	Unknowns (13) as leucine	0.7
Aspartic acid	11.3	γ-Amino-n-butyric acid	3.9
Glutamic acid	10.0		
Valine	6.0	Lysine	2.6
Isoleucine	2.6	Arginine	2.5
Threonine	2.1	Ammonia	1.8
Tyrosine	2.1	Histidine	1.0
Phenylalanine	2.0	Tryptophan	0.5
Serine	2.0	Ornithine	0.2
Proline	1.7	Unknowns (16) as leucine	6.2
Leucine	1.5		
Methionine	1.3		
Alanine	1.2	Total (sum of above)	94.1
Glycine	0.3	Total[a]	110.1

[a] Determined spectrophotometrically (Stein–Moore ninhydrin reagent) as total amino compound content using asparagine as standard.

To obtain an estimate of the column size required and the weight of amino compound mixture that could be produced, a specific example, based on a potato starch plant producing 30 tons of starch/16 h day, can be outlined: assume a waste effluent from the plant to be 6760 gal/h (30 712 l/h) containing 2.6% t.d.s. Protein and inorganic cation and basic amino-acid removal would lower the t.d.s. to 1.4%. Using the plot on Figure 6, it can be determined that with 1.4% t.d.s. feed a treatment rate of 50 g of

t.d.s./h could be employed. From this, using the formula b.v./h = treatment rate/3 × (% t.d.s.), it can be calculated that a flow rate of 11.9 b.v./h could be used. Based on this exhaustion flow rate of 11.9 b.v./h, treatment of this waste would require three columns of approximately 568 gal (2584 l) [75.9 ft³ (2.15 m³)] each for the cation resin. Assuming an amino compound content of 30% of the t.d.s. and a recovery rate of 85% of the amino compounds present, the process would yield approximately 1.6 tons of amino compounds/day. From the regeneration, 2.1 tons of $(NH_4)_2SO_4$ as an 8% solution would also be produced. Since the latter solution contains 21% nitrogen (dry basis) it could be used as a liquid fertiliser.

4.1. Resin life

A sample of IR 120 was sent to the manufacturer after it had undergone about 50 cycles of operation (25 for inorganic cation removal and 25 for amino compound removal). Their evaluation revealed a slight degree of physical breakdown and some evidence of organic fouling as indicated by a decrease in the salt-splitting cation exchange capacity and an increase in the total cation exchange capacity. In summary, the report states that the amount of organic fouling and physical attrition does not appear to be especially great considering the nature of the application. XE 252 was also carried through approximately 75 cycles (50 for inorganic removal and 25 for amino compound removal). This resin was not evaluated by the manufacturer; however, one of the advantages of the macroreticular type resin is its longer operating life. We could detect no decrease in capacity or efficiency in the XE 252 resin after the 75 cycles of operation.

The process outlined in this paper is only part of a complete treatment of starch factory waste water. At this point in the overall process, it can be shown (Table 8) that

TABLE 8. Reduction of t.d.s. and c.o.d. attained by treatment of waste water

| | t.d.s. | | c.o.d. | |
	%	Reduction %	mg/l	Reduction %
Original untreated waste	2.59		25 100	
Waste after protein, inorganic cation (K) and basic amino acids removal	1.38	46.7	14 800	41.0
Waste after amino compound removal	0.95	63.3	10 380	58.6

the c.o.d. (b.o.d.) would be reduced 58.6% from the original untreated secondary waste which is parallelled by a 63.3% reduction in t.d.s. content. The last step of the proposed treatment, the removal of organic acids, would further reduce the total dissolved solids and the c.o.d. This will be described in a subsequent publication.

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